ROTARY KILN SMELTING OF SECONDARY LEAD

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ROTARY KILN SMELTING OF SECONDARY LEAD

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This paper describes the layout and operation of the Pedricktown Plant of NL Industries, Inc., located at Pedricktown, New Jersey, approximately 20 miles from Philadelphia. A description of the complete operation will be given commencing with the decasing facilities, describing the kiln smelting operation and finishing with the refining and casting. The emphasis, however, will be placed upon the kiln smelting which represents a significant departure from conventional smelting, which is predominantly composed of blast furnaces, reverberatory furnaces and short rotary furnaces. The long rotary furnace has some similarities with the short rotary in its chemistry, but in all other respects it is a substantially different technology from any other secondary lead process.

The kiln smelting described in this paper represents a modification of the process employed by Preussag AG, Goslar, Germany, from whom the basic technology was licensed by NL. Some of the major comparisons of this technology with conventional smelting are discussed at the end of the paper.

Battery Decasing

The Pedricktown decasing plant separates the received batteries into acid, grid, large case and separator, middlings fractions and battery paste. Most of the battery acid drains when the battery is received. The battery is then shredded and screened at 5/16". The +5/16 fraction contains grid and large case and separators. These are separated by a magnetite sink float process. The -5/16 contains some non-paste materials which are removed and report to the middlings fraction. The remaining paste slurry is thickened, filtered and dried to make the battery paste product. Figure 1 shows the flow of battery material.

Incoming battery trucks report to the truck dump. There the cab and the trailer are lifted to 60° from the horizontal and the batteries spill out to a receiving area. While the truck is being lowered it is washed with spray water to remove any battery acid. Figure 2 shows the truck dump. Batteries on skids and loosely packed on flat bed trucks cannot be unloaded by the truck dump. These are removed by pushing with a payloader or by fork lift at a separate receiving dock. The sides of the loosely packed flat beds cannot withstand the rush of batteries on dumping and break out creating damage to the vehicle and danger from falling batteries.

The drop during dumping fractures most of the battery cases and a large amount of the acid drains immediately. This flows through a swale into a receiving acid sump and is pumped to storage tanks. The acid is disposed of by waste disposal firms who pump from these tanks to their trucks for transport to their treatment facilities.

An International 515 payloader is used to remove the batteries from the receiving area into one of five receiving bins. These are constructed primarily of concrete with acid brick in areas where most of the drainage occurs. We have observed that acid attack on concrete is not severe until puddling begins.

Batteries to be decased are dumped into the shredder receiving hopper (Figure 3) by a second IH 515 payloader. The shredder is a Saturn Model No. 52-32, 100-HP with MR 375 low speed high torque motor and specially constructed acid resistant alloy cutter teeth. The two opposing rows of teeth rotate at approximately 30 RPM. The blades are driven by a hydraulic system which automatically reverses direction when torque increases above a certain level. This feature allows the hopper to be emptied even when pieces of tramp iron fall into it. The shredder shreds between 1200-1600 batteries per hour depending on the condition of the teeth. We have found it necessary to rebuild them about every six weeks. If this is not done the battery rate drops sharply. Shredder product is nominally minus 2-inch with some plates quite a bit larger in two dimensions.

A 30 inch wide conveyor belt feeds the shredded product through a chute to a 6 feet diameter trommel (Figure 4). This unit is driven by a 25 HP electric motor and has a solid receiving section 4 feet long and a 12-1/2 feet long screening section. The receiving section of the trommel acts as a gentle grinding area in which the material grinding against itself tends to free the metallic grid of any paste adhering to it. The holes in the screen are 5/16 inch in diameter. Water is fed into the receiving section through the chute at a controlled rate and also is sprayed internally on the screen and externally on top of the screen. The trommel rotates at 10.7 RPM and is tilted downward at 7° to the horizontal. In our operating experience we have never had the trommel blind with separators.

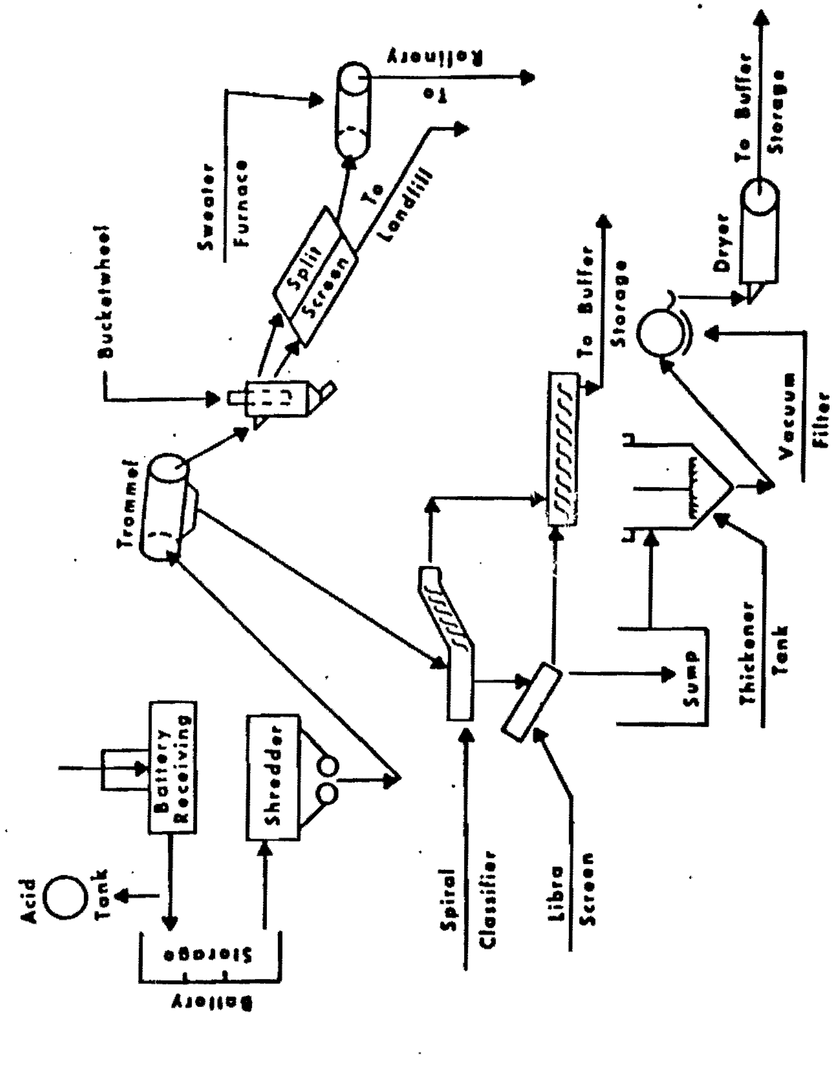


FIG. 1
PEDRICKTOWN DECASING FLOW SHEET

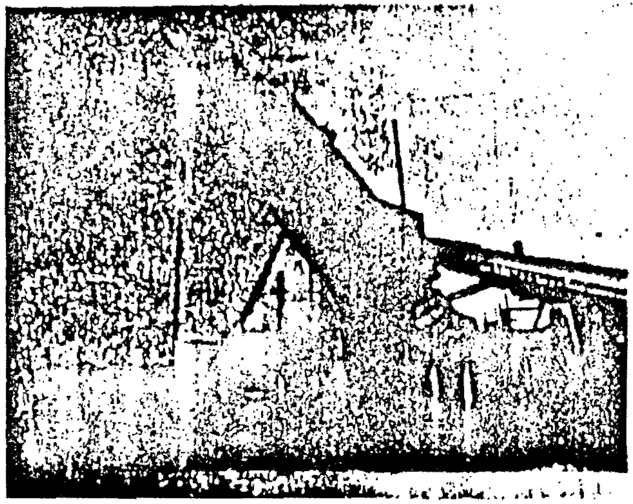


Figure 2 - Truck Dump

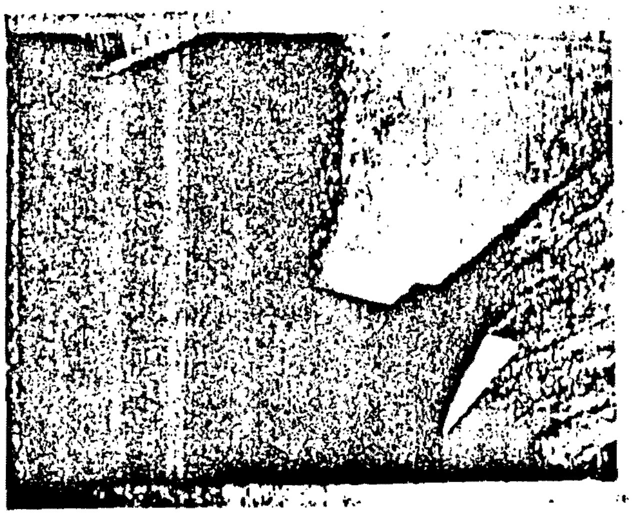


Figure 3 - Shredder Receiving Hopper

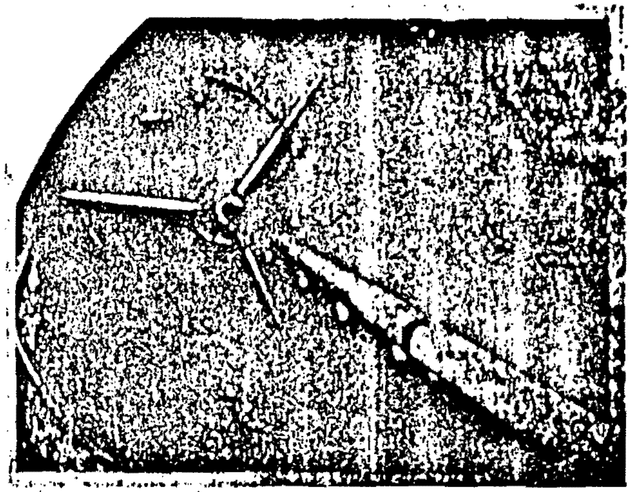


Figure 4 - Trommel

The 5/16" overs fall through a chute into a magnetite heavy media separator. The media is kept between 1.6 and 1.8 specific gravity. The unit is a Humboldt bucketwheel separator and has approximately 1.25 square meters of separating surface. The case and separators float on top of the bath over a discharge chute onto a split screen. The lead grid sinks to the bottom of the bath, is picked up by a revolving bucketwheel, brought to the top and discharged down a chute to the opposite side of the split screen. The separation is complicated by the fact that often times small 1"x1/16" pieces of grid sink past the bucketwheel. For this reason, the unit has been modified so that media and these fines discharge continuously below the wheel itself.

The magnetite used in the sink float is reclaimed and reused. This reclaiming process starts on the split screen. Its first portion is not sprayed. Here much of the heavy media drips off the separated products and drains immediately by gravity into a receiving cone. The heavy media pump then pumps it back into the separator. The heavy media pump is a Wemco Model 6X4WD with 40 HP and is driven at 714 RPM. The farther end of the split screen is washed with sprays which remove the rest of the magnetite from the separated products. They flow by gravity through the screen into the light media receiving cone and into the light media pump. It transfers the light media to a magnetic separator which reclaims the magnetite from the water. The discharge from the magnetic separator drops by gravity into the heavy media cone.

The heavy media sinks fall from the split screen through a chute onto a conveyor belt which delivers them to the sweater furnace. This is a rotating tube furnace 4 feet in diameter and 20 feet long, which is fired from the discharge end by one burner which also has the ability to cool by blowing air through the nozzle without flame. Grid metal melts in the furnace. Off-gases are treated in a baghouse. About 85% of the feed reports as lead and 15% as dross. The lead buttons are removed for use directly in the refining area. The dross is transported to the kiln area for smelting. We have found that the amount of plastic in the grid portion influences the operation of the sweater greatly. Excessive plastic requires the unit to be cooled.

The washed case and separator material is delivered by conveyor to a storage pile. We are currently selling this material to a firm who is reclaiming its plastic content and extruding this to make plastic product for sale and manufacture of specialty items.

All the -5/16" which goes through the trommel screen is eventually smelted. The equipment used subsequently for processing removes the water used in screening in the trommel screen.

The first step in water removal is to remove the unpumpable material to form a middlings fraction. This is done using the spiral classifier followed by a flat screen. The spiral classifier removes that material which sinks so quickly that it cannot be pumped. The water content is approximately 15% on discharge. The overflow contains the battery paste and -5/16" overs case and separators. The latter are removed on a flat screen with approximately 44 square feet of surface area. Both the spiral classifier and flat screen discharges go to a long screw which delivers the middlings to the buffer storage room for kiln smelting.

The screen unders are battery paste slurry with between 10-15% solids. These fall by gravity to a 50 HP pump which transfers them to a thickener. The thickener is 30 feet in diameter by 9-1/2 feet deep and has an automatic torque lifting sensing device on the rake.

The thickened battery paste flows out of the bottom of the thickener through one of two 5 HP Moyno pumps which are made using a chrome-plated tool steel type rotor, natural rubber type stator, and pump the battery paste through a 1-1/2" line to a rotary drum filter. The slurry is usually between 60-70% solids once it leaves the thickener. The line to the filter contains a nuclear density gauge which continually measures the density of the slurry. The filter is an EIMCO filter 10 x 12 feet in size, rests in a tub, and is fitted with an agitator to keep the slurry in suspension. It is operated without an overflow and material is fed to it intermittently to keep the level in the filter within about a foot of the top of the tub. The filter is run between 19-22" mercury vacuum. The vacuum system consists of a filtrate receiver connected through a barometric seal to an output sump and a 60 HP Siemens vacuum pump. The filter drum typically has a cycle time of 3 minutes and the cake is released by using a scraper blade and a small amount of snap blow air. The cake is usually released at about 10-15% moisture. It is usually about 1/4" to 1/2" thick.

The filter cake falls into a receiving screw, and is conveyed to a screw which feeds it to a 4 feet diameter by 24 feet long rotary drum drier. The rotary drum drier is fitted with a scraper to prevent accumulation of material inside the drum. The dried material contains 6-8% moisture and consists of nodularized material (pellets) usually between 1/2" and 1/4" in diameter and containing 15-20% fines. The discharge is conveyed by a ribbon screw conveyor to the buffer storage building. The drier off-gasses are treated in a Ducon scrubber to remove particulates.

The thickener serves as the plant's water reservoir. The water for the sprays for the trommel screen, the spiral classifier, the libra screen and the split screen is supplied by the thickener overflow. It is then pumped to the sprays or if there is excess water to a holding inventory tank. The plant has numerous valves for floor wash down and cleanup all of which are done with water from the thickener overflow. All washup water eventually ends in the bottom floor of the building and drains from there into a sump pump which pumps it over the magnetic separator and then into the thickener.

The plant is operated 3 shifts a week, 5 days a week on a 24-hour basis. The department employs a superintendent, three foremen and six hourly personnel per shift. One of these is used to load the batteries into the shredder; a second to monitor the equipment before the heavy media section; the third to monitor the operation of the bucketwheel separator; a fourth to monitor and operate the thickener, filter and drier; a fifth as a utility man to provide for relief breaks and lunches; and the sixth to provide for absentee replacement and cleanup.

The most significant costs in operating the plant are depreciation, maintenance, and the cost of disposing of waste acid and decasing effluent. The need for maintenance is continual. This facility uses many pieces of equipment in one line and without much surge. We have been able to obtain 70% operating factor during the last year and believe it will be possible to improve this to 80-85%. That improvement depends on careful preventative maintenance. We pay very careful attention to the amount of gland water used on our pumps as we find that attention pays off in greatly reduced effluent haulage cost.

Kiln

The Pedricktown rotary kiln is a 177 foot long, 10 foot diameter used cement kiln converted to lead smelting specifications (Figure 5). The furnace is inclined slightly to the horizontal and contains 392 tons of

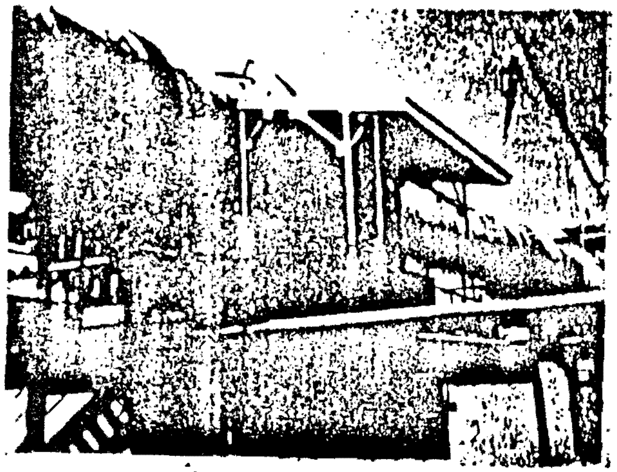


Figure 5 - Kiln

refractory made up of alumina brick in the feed and preheat zones, burned magnesite-chrome brick in the reaction zone, and the entire length is backed up by 3 inches of insulating firebrick. The discharge end of the kiln is narrowed for 6 feet 3 inches with the basic brick to form a dam (corbel) to allow for the collection of metal. Bricked working diameter of the furnace is 8 feet at the feed end and 4 feet at the discharge end.

The kiln is fired by a 35 million BTU oil burner positioned at the discharge end and angled forward enough so that the flame strikes the edge of the bath just behind the corbel (Figure 6).

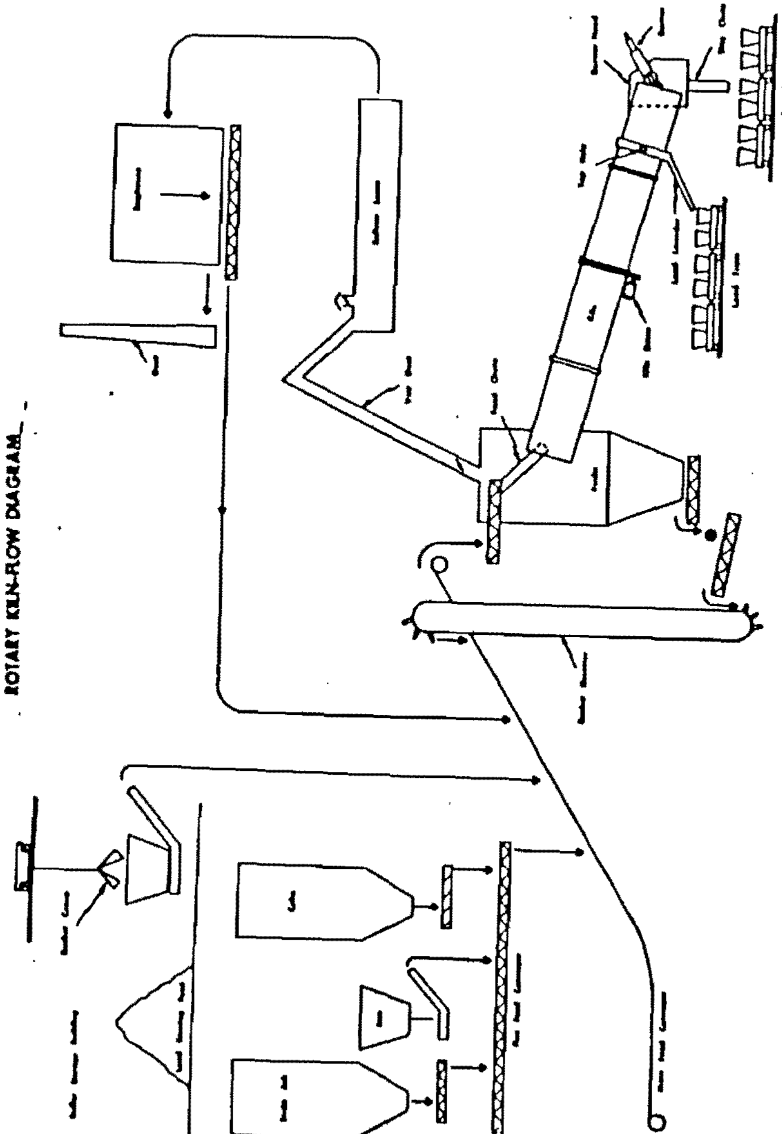
The rotary kiln sits on three large concrete piers, and each pier has two trunnion rollers upon which the kiln tires rest. The roller bearings are lubricated through a recirculating oil system, which has provisions for maintaining the oil temperature at 100-120°F. The kiln is rotated by means of a large ring (bull) gear attached to and encircling the outside of the kiln. This gear is driven by a pinion drive gear, which is in turn driven through a water-cooled magnetic coupling clutch by a fixed speed A.C. electric motor. Rotational speed variation through a range of 0.3 to 1.1 revolutions per minute is obtained by varying the current to the magnetic clutch. An auxiliary gasoline engine is provided as a backup source in case of electrical failure.

Lead-bearing feed material is stored in an enclosed bin that is kept under negative pressure. A bridge crane with a 1-1/2 yard capacity bucket operating within the building delivers the feed to a 15-ton capacity hopper. The hopper is emptied by the action of an apron feeder pulling material away from the opening at the hopper bottom. The apron feeder conveys the material to the kiln feed conveyor, a 150 foot long completely enclosed belt conveyor set at a 17° angle. At the top of the conveyor, the material is discharged into the kiln via an angled feed chute or a feed screw, depending on the physical nature of the material being used.

Petroleum coke and soda ash are stored in enclosed bins having a capacity of 260 and 409 tons respectively. Each of the bins is equipped with individual piping and baghouse systems for blowing coke and soda ash from pressurized delivery vehicles into the storage bins. Both bins have vibrating bottoms that assist the movement of the bin contents into screw conveyors which are operated by variable speed D.C. motors. The variable speed screws convey to a common flux feed screw, which in turn discharges onto the aforementioned kiln feed conveyor. Cast iron chips are fed from a 10 ton V-bottomed hopper and, as they settle, are pulled from the bottom of the hopper by an apron feeder and deposited into the flux feed screw. The cast iron chips are mixed with the petroleum coke and soda ash in the screw and are discharged onto the kiln feed conveyor.

The rotary kiln metallurgical gas stream is cleaned by an 18 cell Norblo baghouse powered by a 150 HP fan capable of discharging 38,000 CFM. Each cell contains 78 acrylic fiber bags having a permeability of 40 $ft^3/ft^2/min$. The kiln is drafted from the charging end through a large gravity settling chamber known as the "fuchs". The dust that drops out in the fuchs funnels into a screw conveyor, which carries it back to the kiln feed conveyor by way of the recovery loop. The recovery loop is comprised of a horizontal screw conveyor, a rotary valve, an inclined screw conveyor, and a bucket elevator. The gas stream from the fuchs is first pulled through a vee duct cooling tube and then through the balloon flue (Figure 7), expanded duct with a screw conveyor mounted on the bottom, prior to entering the baghouse.

ROTARY KILN-FLOW DIAGRAM



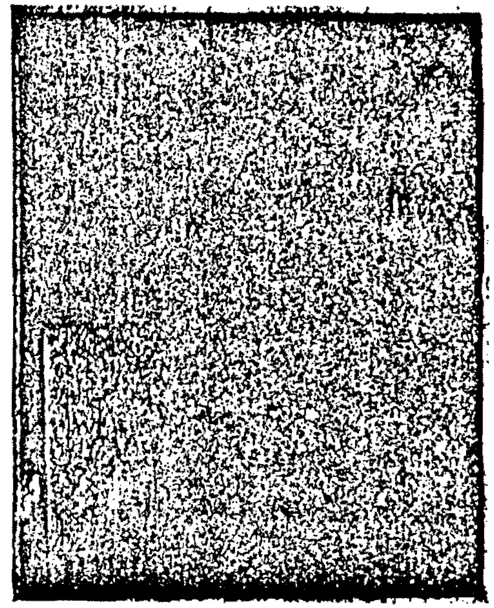


Figure 6 - Kiln Burner

Figure 7 - Vee Duct
Balloon Flue

Mounted on the balloon flue is a bleed air damper, its function to allow outside cool air to flow in to maintain the proper baghouse inlet temperature. The damper is operated by a Leeds and Northrup controller and is capable of operating in either the manual or automatic mode. Negative pressure in the kiln is controlled by a damper mounted on the outlet side of the fuchs at the base of the vee duct.

A 24-cell Norblo baghouse handles the sanitary gas cleaning requirements for the kiln and the refining department. Sanitary hoods are provided over the lead launders at the discharge end of the kiln (firing hood), over the slag and lead trains, and over the lead tapping section. The dust that is collected from the kiln operation, both from the metallurgical and sanitary systems, is returned to the kiln feed conveyor through a screw conveyor system.

The slag, which forms on the surface of the metal, overflows the corbel continuously through a chute and is collected in slag pots. Two slag pots sit atop each car of a five car cable-drawn train. Lead is tapped periodically by stopping the kiln, breaking open the tap hole, then rotating the kiln until the tap hole points downward. Lead is collected by means of refractory lined launder chute which directs the flow into botton molds placed on a cable-drawn lead train.

All controls and instrumentation that support the rotary kiln operation are housed in one of two air-conditioned, dust-free control rooms. The feed control room (Figure 8) is located within the enclosed negative pressure bin and contains the crane controls, the start/stop controls and indicator lights for all feed and recovery system screws and belt conveyors, the rheostats that control the variable feed screws and conveyors and the controls for the pneumatic coke and soda ash handling system. The kiln control room, located in the tapping area, houses all kiln and baghouse temperature indicators and recorders, start/stop controls and indicator lights for kiln systems and draft control instrumentation (Figure 9).

Start Up

The time requirement for kiln start up varies depending on the condition of the refractory. In the case of a newly rebricked kiln, the fuchs and firing hood are dried out for a two-day period by placing salamanders inside them. At the end of this period, the main burner is turned on and the furnace temperature is raised 100°F per hour to 1200°F. Once the temperature has reached 1200°F, it is held for an additional 12 hours to permit the brickwork to get uniformly hot out to the steel shell. At the end of this "soak" period, the kiln temperature is again raised 100°F per hour until the temperature reaches 2400°F. During this last 12-hour period, the kiln is rotated one-quarter turn every 15 minutes. At the end of this heatup period, feeding begins at approximately 35% of capacity for 12 hours, after which it is increased to 65% for 12 hours and thereafter to designed capacity. Start up with used refractory involves heating the kiln without rotation to process conditions over an 8-10 hour period. When the shell temperature reaches 250°F at the tap hold, the kiln is rotated 180°F every half hour for approximately 4 hours. At this point, feeding begins and proceeds as described above.

Technical Training

The training of personnel for both the kiln and decasing operation was accomplished by the central technical training department via a Criterion

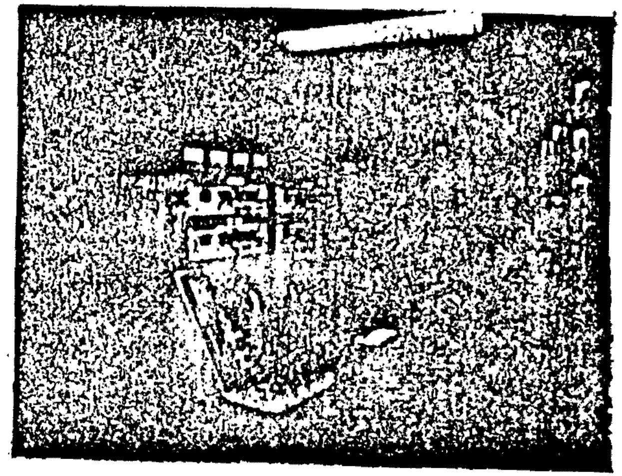


Figure 8 - Feed Control Room

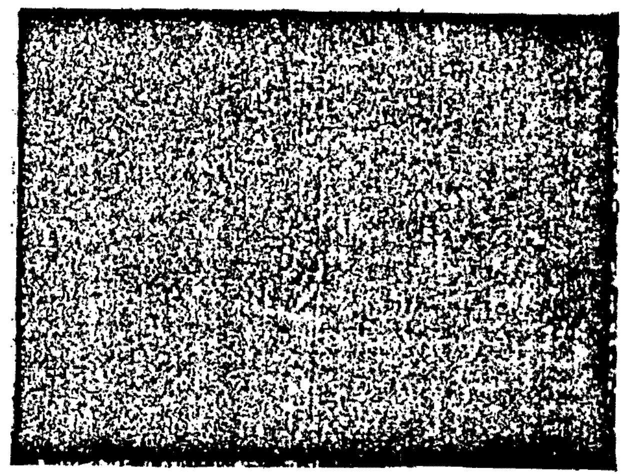


Figure 9 - Kiln and Baghouse Temperature Indicators & Recorders

Referenced Instruction Program. CRI training is a course of instruction in which the subject matter is taught a small portion at a time with the requirement that the trainee demonstrate his understanding of that one small portion before proceeding to the next higher learning step. The program proved to be very effective; operators were well versed with the equipment, contingency procedures and operating perimeters, and above all no accidents were suffered during the three-month start up period.

Manpower Requirements

The kiln is operated on a three shift per day, seven day per week schedule. A tapper, charger, slag handler, lead train operator, baghouseman and relief operator per shift comprise the hourly work.

A smelting manager is responsible for the overall operation and has four shift foremen to supervise the furnace.

Maintenance

Ninety percent of all kiln maintenance and repair is performed by the plant maintenance department. One maintenance mechanic per shift is assigned to the kiln, each performing a total of 91 equipment checks and lubrications. Rebricking and the large fabrication and/or repair jobs that are conducted during scheduled shutdowns are contracted out.

Since the kiln start up in April of 1978, there have been four shutdowns to make repairs to or replace refractory. Refractory experiences are outlined in Table 1.

Operation

As is the case with all furnace operations, there are certain important aspects which must be monitored and controlled via instrumentation and operator observation. With the kiln operation, this can be broken down into four major headings: the feed system, burner system, off gas system, and the kiln. Each major heading is then sub-divided as follows:

The feed system, as previously mentioned, is made up of two primary feed systems to include lead bearing feed and flux feed. Both systems, as will be explained further later, are set by a potentiometer and re-calibrated at each feed rate change. Once calibrated, the controls are locked at the panel board and a reading is taken once per hour to insure accuracy.

The burner system consists mainly of oil pressure valves and air rate control dampers, which are set for maximum burner efficiency, and monitored via gauges at each critical point. In addition, an oil rate meter is utilized to monitor fuel consumption and aid us in maintaining an energy efficient system.

The kiln off gas system is equipped with draft control, temperature monitoring and environmental controls. To enable us to monitor temperatures, we have installed a 12 point recorder which records fuchs temperature, top and bottom baghouse temperatures and stack temperature. Individual temperature meters have also been installed to monitor the baghouse inlet and burning zone temperature. To cover draft requirements and environmental needs, we have incorporated a recording meter and photohelixes for draft monitoring, a combustion meter for gases, and an opacity meter for monitoring

Table 1

Kiln Refractory History

	Rebricking Period	Short Tons Produced During Campaign	Cause of Failure	Scope of Repairs
Initial Lining	Installed 8/77	—	—	—
First Rebricking	8/23-9/5/78 (13 days)	7,898	Normal deterioration of refractory. Shell temp. in reaction zone rose to critical levels.	Replaced entire corbel plus 14' of reaction zone. Due to severe spalling, portion of alumina brick beyond reaction zone was replaced with magnesite chrome. 13' of alumina brick in feed zone was replaced due to crushing & radial shifting.
Second Rebricking	10/27-11/2/78 (7 days)	5,141	Corbel deterioration with top dam bricks broken away and lead penetrating through lower courses.	Replace corbel.
Third Rebricking	4/7-4/22/79 (15½ days)	19,241	Normal deterioration of refractory.	Replaced entire corbel & reaction zone. Improvements made include: (1) Added insulating brick under steel retaining rings for greater insulation in critical areas. (2) Tighter refractory placement with reduced longitudinal expansion spacings. (3) Tighter refractory joints with mortar fill in critical and vulnerable locations. (4) Straightened & aligned moon castings for greater support.
Fourth Rebricking	7/6-7/9/79 (4 days)	937	Excessive temperatures created refractory deterioration in top courses of corbel bricks. Problem could not be remedied by spot repair.	Replaced corbel with even tighter expansion joints.
		Through 7/22/79 12,117		

stack emissions.

The kiln itself is equipped with rotational speed control and a monitoring meter, a drift monitor alarm, and cooling water and lube oil temperature meters for monitoring the bearings.

Several other critical functions not covered by instrumentation as such are safeguarded by alarm systems. Typical examples of these alarms are: vee duct high temperature, baghouse inlet high temperature, flame failure, clutch cooling water low pressure, kiln drive motor stopped, etc.

As with any new furnace, unexpected operational problems develop that require perseverance on the part of the furnace staff and hourly personnel to analyze and overcome procedurally. A discussion of some of these difficulties follows.

The original feed system at start up, for the rotary kiln was a gravimetric system using weighbelts combined with various types of transition conveyors. This system was, and still is, considered the optimum system for charging the kiln. However, early in the start up, it became apparent that the system, as designed, was too sophisticated for reliable day-to-day operation in a smelter environment. It wasn't long before the weighbelts were taken out and the feed system was converted to a simple volumetric basis.

Operating a volumetric feed system required that an accurate means of calibrating feed rate be developed. Our present system utilizes a variable potentiometer which controls the speed of each individual feed conveyor. This potentiometer is calibrated by the simple expedient of running the system at a particular setting for a set period of time with the feed diverted to a drum. The feed thus collected is weighed and the rate is calculated. This is done a number of times at different settings and the results are plotted. Using the reference calibration curves thus obtained, it is a simple matter to change charge composition when required.

During the 16 months of kiln operation, the composition of the charge to the kiln has varied considerably. Some of this was expected, and planned campaigns to run particular lead-bearing feeds have been scheduled. However, some of it is due to the natural variation that occurs in scrap lead feed. The kiln is a dynamic smelting system and, while not as sensitive as a blast furnace, changes in charge composition must sometimes be made.

Care must be taken however to distinguish between those conditions which are transient in nature and do not require charge adjustments and those which do. Adjustments to the ratio of fluxes are most common, particularly soda ash and coke. These adjustments are based on several factors: slag chemical analysis, slag pool appearance and general kiln parameters. Adjustments in the rate of feed is usually dependent on the type of scrap being fed to the kiln.

The role of the burner in kiln smelting is only now beginning to be fully appreciated. The burner's main role is to initiate the smelting reactions at start up through the ignition of the coke in the charge. Once these reactions are underway, the oxidation of the coke and the exothermic heat from the lead oxide reduction supplies the bulk of the necessary heat to the kiln. The burner thereafter is mainly used for slag control. Minor adjustments are made in the burner to keep the slag within a specific viscosity range. These adjustments can involve changes in flame characteristics and/or angular position.

Slag viscosity control is important for the clean separation of lead and slag. A viscous slag can carry a significant amount of lead prill out of the kiln. It also causes a transport problem - building up on the corbel face and clogging the slag chute.

Too thin a slag can signal the beginning of problems within the kiln. The flux ratio may be incorrect or the smelting zone may be moving. The smelting zone can and does shift within the kiln. Factors such as feed rate, coke level, draft control and feed type can cause these shifts. Movement of the smelting zone can be followed by monitoring the temperature readouts at each end of the kiln.

The kiln draft is controlled by the reciprocal adjustment of the fuchs damper located in the vee duct and the bleed in air damper on the balloon screw. Automatic controllers are provided for these two dampers. However, their operation must be periodically monitored to see that they stay within the effective controller range. Since there are almost an infinite combination of settings for these two dampers which can yield the same draft and temperature conditions within the kiln system, they have a tendency to drift until they are out of control. The control of these two functions is critical for maximum kiln production.

As previously mentioned, the rotary kiln at Pedricktown is a used concrete kiln. It is mounted, out in the open, on three concrete support piers. Because of the combined weight of the refractory and the lead charge (about five times denser than concrete) and the marginal support, extra care must be taken to keep the kiln from warping and/or drifting. The extreme load also makes lubrication of the trunions and bearings extremely critical.

As a result, once the kiln is fired up and up to operational heat, it is never fully stopped for any length of time (about 15 minutes maximum). An idling procedure has been instituted wherein the kiln is slowly rotated or given a periodic quarter turn during any temporary "hold" condition. Should the hold be prolonged, the kiln is emptied of slag and lead and gradually cooled down while being rotated.

Start up of the kiln proceeds differently depending on whether or not the start up follows a rebricking. Following a rebricking, the kiln is heated up very slowly to drive off the moisture on the refractory. As the bricks expand and lock in place, the kiln is rotated slowly and the heating is continued until it is up to near operation temperature. When this point is reached, feeding is commenced.

The original lead tapping procedure called for a receiving kettle mainstay with a manually rotated launder chute filling button molds as a backup. This concept was abandoned prior to start up due to the anticipated difficulty of pumping "dirty" bullion out of the receiving kettle.

A lead carrousel was designed and used successfully for some 10 months. However, mechanical difficulties became an increasing problem. Currently a lead train, virtually identical to the one used for slag, has replaced the carrousel and is operating satisfactorily.

<u>Charge</u>

Daily kiln tonnage fluctuates significantly as a function of charge. Three basic charges are utilized, depending on antimony requirements in the generated metal: pellets/middlings, plant scrap, and occasionally 3:1 grid metal/pellets. The pellets/middlings charge has produced a daily high of 225 tons but normally averages 200 tons per day with bullion at a >1.25% antimony level. A high of 288 tons has been realized on plant scrap, the average daily tonnage being 225 with an average antimony content of 6%. The 3:1 grid metal/pellets charge averages 180 tons per day, the high tonnage being 200 and the average antimony content runs 3%.

Laboratories

The chemical laboratories at Pedricktown are located in the main office building, while the assay room is located in a wing off the refining building. The lab is equipped with a Baird-Atomic 1 meter, Spectromet 1000, direct reading spectrometer, a Varian Techtron Model AA6 atomic absorption spectrophotometer with a M-80 gas box, a Leco Model 532-000 sulfur analyzer, a Leco Model 761-100 carbon analyzer and the conventional wet chemical facilities.

The laboratory's major emphasis is on kettle process control samples for which the spectrometer and atomic absorption spectrophotometer are most highly utilized. Incoming drosses, batteries and metal scrap are assayed as required. Daily samples of kiln slag and periodic samples of feed materials and fluxes provide control for the kiln operation.

Kiln Chemistry and Reactions

During the design and construction of the Pedricktown kiln, a computer model of the process was constructed in order to better define the process parameters. We will not here go into any details regarding the model, since this will follow as the subject of a separate paper. However, in order to get up the main feature of the model, namely a mass and heat balance simulation of the kiln, we had to arrive at an understanding of the kiln reactions as functions of distance from the feed end. This understanding is described below.

The feed to the kiln comprises the lead-bearing portion of the charge, composed of the output from the decasing operation, combined with other lead scrap, finely divided petroleum coke, case iron chips, and soda ash, to name the principal constituents. The amounts of coke, iron and soda are adjusted to suit slag chemistry and also temperature. Equations 1 through 8 describe the basic smelting reaction.

$$3\,C + 2\,PbSO_4 + \frac{Na_2CO_3}{Flux} \longrightarrow 2\,Pb^0 + Na_2S_2O_3 + 4\,CO_2 \quad (1)$$

$$5\,C + 2\,PbSO_4 + \frac{2\,Na_2CO_3}{Flux} \longrightarrow 2\,Pb^0 + 2\,Na_2S + 7\,CO_2 \quad (2)$$

$$PbSO_4 + 2\,C \longrightarrow PbS + 2\,CO_2 \quad (3)$$

$$C + 2\,PbS + \frac{2\,Na_2CO_3}{Flux} \longrightarrow 2\,Pb^0 + 2\,Na_2S + 3\,CO_2 \quad (4)$$

$$PbS + \frac{Fe^0}{Flux} \longrightarrow Pb^0 + FeS \quad (5)$$

$$PbO_2 + C \longrightarrow Pb^0 + CO_2 \quad (6)$$

$$2\,PbO + C \longrightarrow 2\,Pb^0 + CO_2 \quad (7)$$

$$\frac{Na_2CO_3}{Flux} \longrightarrow Na_2O + CO_2 \quad (8)$$

It can be seen that the coke acts primarily to reduce the lead oxides to metallic lead and to reduce the sulfate to sulfide. Additionally, coke also undergoes the following reaction:

$$C + O_2 \longrightarrow CO_2 \quad (9)$$

and we have found in practice that this reaction plays an important part even though heat is provided at the front end of the kiln with a burner. The burning of the coke is experienced over the entire length of the kiln even up to the point where the coke may be seen burning on the slag layer as slag pours over the corbel. The reactivity of the coke is an important factor, and we have found petroleum coke to be most suitable. The sodium carbonate reduces the lead sulfide to lead, and the other reaction product varies from Na_2S all the way to Na_2SO_4 with several different intermediate compounds such as sodium thiosulfate also being found. Since the predominant species are sodium thiosulfate and Na_2S, the proportions of these two constituents are used as indicators of the state of oxidation of the slag. The small amounts of sulfur in the coke and other incidental sources also react with sodium carbonate in the same way. An important function of the soda is also to reduce the levels of sulfur oxides in the off gases. This "gettering" action causes the sulfur dioxide in the off gases to be well below 200 parts per million. Some unreacted soda also escapes with the flue dust and is returned to the kiln when the dust is recycled. The airborne sodium carbonate also exerts "gettering" action upon some chlorides that happen to be present in the air stream. These chlorides are generally in the form of HCl evolved from the burning of PVC separators.

The action of the cast iron is to act synergistically with the soda to reduce the lead sulfides to lead. The proportions of iron and soda are adjusted so that the compositions of the slag are such as to be in the low melting portions of the eutectic valleys.

The heat for the kiln reaction comes from both the coke and the fuel oil being burned. In the early portions of the kiln where the materials are solid, heat transfer from the hot gases to the solids is affected by the rate of rotation, since increasing the rate increases the turning over of the surface solids, thus transferring the heat to the layers below. At the tapping end of the kiln, the temperature is controlled primarily by adjusting the burner. Although from the standpoint of entrained metallic lead it is preferable to have slag as fluid as possible, an intermediate viscosity is preferred in order to minimize the refractory wear.

The majority of the slag is composed of the sulfides and oxides of sodium, iron and lead, together with silica, alumina and other oxidic constituents present in the feed materials. Also present to levels up to 20% is unburned coke. Of the compounds mentioned above, the sulfides predominate; although in the case of sodium, there also exist thiosulfates. The presence of the high concentration of sulfides allows this material to be alternately called a matte rather than a slag. The oxides in sulfides will not separate out into two different layers as they do in the blast furnace. The nonmetallic lead present in the slag is extremely insoluble in water because the predominant specie is PbS. The slag is hygroscopic and this has to be taken into account when running slag analyses. Furthermore, due to the presence of the entrained carbon, this slag must be handled and disposed of using special techniques, which are simple but absolutely necessary. A discussion of the methods employed to properly handle slag is contained in a patent that is expected to be issued shortly.

Refining and Casting

The Pedricktown refinery was constructed in 1972 and was not altered during the kiln construction and decaser revamp in 1977-78. The refinery consists of twelve 90-ton kettles arranged in two groups of six with an aisleway and 100 mold Wirtz casting machine separating the two. Plans originally called for reserving one group of six kettles for soft lead production and the other group for antimonial lead production. Due to higher demand for soft lead and soft lead based grid alloys, nine kettles are now designated for "soft lead use only". Soft lead is manufactured from low antimony kiln metal by oxidation with air, intermetallic impurity removal and caustic-sodium-nitrate treatment. Antimonial lead is produced from 2-1/2 to 3% kiln metal or sweeter metal.

The refining kettles are constructed from ASTM-A285C firebox steel, 1-1/2 inches thick. They have straight sides, 38 inches length and an elliptical bottom. All kettles are stress-relieved at 1100°F by the manufacturer. Kettle settings consist of a steel shell lined with 3 inches of insulating castable refractory and 13-1/2 inches of firebrick.

The floor of each setting is made up of a layer of 3 inches castable refractory, a course of 4-1/2 inch brick and a layer of sand. Fumes and/or unburned combustion gases in the setting are carried off by a ventilating flue system.

Each kettle is equipped with a North American Mfg. Co., Model No. 5795-54-8A nozzle-mix type oil burner rated at 10 million BTU/hour and a full flame safety system.

Drossing is conducted using an automatic drossing machine which operates under ventilated kettle hoods.

All mixers are mounted on kettle hoods and are of right angled drive design, driven by belts and powered by 30 HP motors. Three bladed impellers are used exclusively.

Lead pumps are comprised of two types: transfer-pumps which are used to move molten lead from kettle to kettle and casting-pumps. All pumps are of centrifugal design and are driven by fixed AC electric motors. The casting pump that feeds the Wirtz casting machine is made to operate as a variable speed pump by varying the frequency at which the motor operates. This is accomplished by plugging the pumps into a "black box" speed control panel and dialing the speed required.

Discussion

Comparison of Rotary Kiln Smelting with Blast Furnace

We will discuss here some of the major differences between these two types of smelting. Although both methods employ continuous smelting, in the kiln process the slag is tapped continuously while the metal is tapped periodically, whereas in the blast furnace the situation is exactly reversed. Major differences, too, lie in the chemistry and the ease of operation. The rotary kiln is, without question, a simpler furnace to operate in that individuals can be trained expeditiously; and there is required a minimum of experiential knowledge of the type required in the blast furnace. This is partly because there is a higher degree of automation in this furnace and partly because the kiln is a more stable furnace in that departures from normalcy do not generally have catastrophic effects.

In a blast furnace, furnace shutdown, or lost time burn down, can be caused by the following situations: sow formation due to a high iron condition, excessive unsmelted material due to low iron or coke, improper charge distribution, hands and accretions in the shaft, extended elevation of the smelting zone and high back pressure. The last item can have a variety of causes, including presence of too many fines on the charge. In contrast, the kiln operates efficiently with fines; and an extended shutdown can only be caused by a few events.

In recent times, the extensive use of PVC separators has effected blast furnace operations adversely because the volatile lead and iron chlorides form a reflux loop in the furnace resulting in operating difficulties and also lead lost in slag (or lead chloride). In the kiln, the chlorides easily react with the soda and the resulting NaCl product is not detrimental as a slag constituent.

Overall manpower requirements are lower on the kiln when compared on a tonnage basis. Also the tasks are simpler and less intensive in that a majority of the operations are on a timed schedule, whereas in a blast furnace the slag tapping is often required to be on the basis of visual observations (requiring experience), and on the same furnace tapping intervals can vary from 10 minutes to 30 minutes depending upon furnace conditions.

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